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Glass Transition and Crystallization Behavior of Binary Divalent Metal Vanadate Glasses

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The glass transition and crystallization behavior of various binary divalent metal vanadate glasses have been investigated by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The values and compositional dependences of the glass transition temperature, T_g, and the crystallization temperature, T_x, of alkaline earth vanadate glasses were similar to each other.

The T_g's of lead vanadate glasses were low compared with those of alkaline earth vanadate glasses. The results obtained were interpreted in terms of the difference in the vanadate groups contained in these glasses. It was noted that as for $50MO{\cdot}50V_2O_5$ glasses (M=Sr, Pb), the process of crystallization depends on the kinds of the vanadate groups present in the glasses.

KEY WORDS: Structure of binary divalent metal vanadate glasses/ Glass transition/ Crystallization

1. INTRODUCTION

It is of practical and scientific importance to know the glass transition and crystallization temperatures, and the softening point of glass. These properties are directly related to the thermal stability of glasses. They also sometimes give significant information concerning the network structure of glasses.

It has been shown from ^{51}V NMR study[1,2] that the network structure of divalent metal vanadate glasses mainly consists of VO_4-tetrahedra, and is very similar to each other except for the local environment of divalent metals. It is also found that the local environment around vanadium atoms is infiuenced by the presence of the second neighboring divalent metal, as evidenced by the ^{51}V NMR isotropic chemical shift. Therefore, it is interesting to know the effects of the kind of divalent metal (M) and the MO content on the thermal properties of glasses, such as glass transition and crystallization temperatures, and the crystallization process.

In the present work, the glass-forming region of various binary divalent metal vanadate glasses has been first established, and the glass transition and the crystallization behavior have been investigated by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The results obtained have been discussed in relation to the glass structure revealed by previous ^{51}V NMR study.[1,2]

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2. EXPERIMENTAL

Compositions of the glasses used in the present work are shown in Table 1. Binary divalent metal vanadate glasses of the compositions $xMO\cdot(100\text{-}x)V_2O_5$ (M=Ca, Sr, Ba, Pb, x=30, 40, 45, 50, 55) were prepared using reagent-grade V_2O_5, $CaCO_3$, $SrCO_3$, $BaCO_3$, PbO chemicals supplied by Nacalai Tesque. Starting materials were well mixed and then melted in a Pt-5%Au crucible in an electric furnace at temperatures of 950 to 1,100°C. The melts were poured onto a brass plate and immediately pressed by another one. For $50CaO\cdot50V_2O_5$, $55SrO\cdot45V_2O_5$ and $55PbO\cdot45V_2O_5$ the crucible containing a small quantity of melt (~1 g) was directly soaked into ice water to cool down more quickly. DSC curves were recorded in air for bulk samples of about 20 mg. The scans were made at 10°C/min using a Rigaku Thermoflex TG8110 calorimeter. The glass transition temperature, T_g, and crystallization temperature, T_x, were estimated from the DSC curves. The glass samples 1–2 mm thick was heat-treated in an electric furnace in air to identify the precipitated crystalline phases by XRD, using a Rigaku Geigerflex RAD-IIA diffractometer.

3. RESULTS

3.1 Glass-forming region

Table 1 shows the glass-forming region of the glasses, in which all the marks except crosses mean glasses to be formed. The triangles denote that glasses cannot be prepared by the usual vitrification method with 10 g batch but can be prepared by rapid cooling of a small quantity of melt (~1 g). The closed circles denote that the glasses are apt to be hydrated by moisture in ambient atmosphere. It is seen that the glass-forming regions are almost the same irrespective

Table 1. Glass forming range of binary vanadate glasses melted at 950–1,100°C.

MO /mol%	Ca	Sr	Ba	Pb
55	×	△	×	△
50	△	○	○	○
45	△	○	○	○
40	○	○	○	○
30	●	○	●	○
20	●	●	●	●

×: crystal, △: glass and crystal, ○, ●: glass, ●: These glasses are subject to the moisture attack.

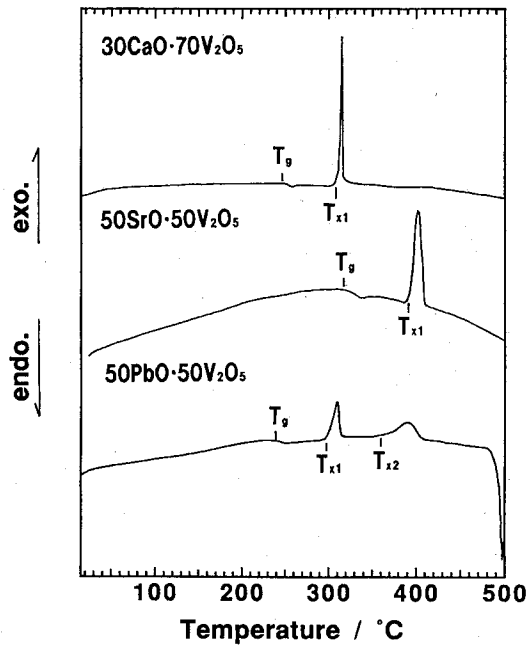

Fig. 1. DSC curves of $30CaO70V_2O_5$, $50SrO\cdot50V_2O_5$ and $50PbO\cdot50V_2O_5$ glasses.

of the kind of the divalent metal, although the sensitivity to moisture attack is slightly different from each other.

3.2 Glass transition and crystallization temperatures

In Fig. 1 typical DSC curves taken for $50SrO{\cdot}50V_2O_5$ and $50PbO{\cdot}50V_2O_5$ glasses are shown. All lead vanadate glasses and several alkaline earth vanadate glasses have more than two exothermic peaks. The glass transition temperature, T_g, and the crystallization temperature, T_x, are shown in Table 2.

Table 2. The glass transition temperature (T_g) and the crystallization temperature (T_x) of binary vanadate glasses.

Glass sample	T_g (°C)	T_x (°C)
$50CaO{\cdot}50V_2O_5$	314	378
$40CaO{\cdot}60V_2O_5$	276	314
$30CaO{\cdot}70V_2O_5$	247	312
$55SrO{\cdot}45V_2O_5$	348	399
$50SrO{\cdot}50V_2O_5$	319	396
$40SrO{\cdot}60V_2O_5$	275	367
$30SrO{\cdot}70V_2O_5$	251	294,391 (w)
$50BaO{\cdot}50V_2O_5$	318	382,422 (w)
$40BaO{\cdot}60V_2O_5$	271	355
$55PbO{\cdot}45V_2O_5$	242	297,359 (w)
$50PbO{\cdot}50V_2O_5$	240	298,360
$40PbO{\cdot}60V_2O_5$	222	256,303 (w)
$30PbO{\cdot}70V_2O_5$	214	237,405 (w)

w : The intensity of the exothermic peak is very weak.

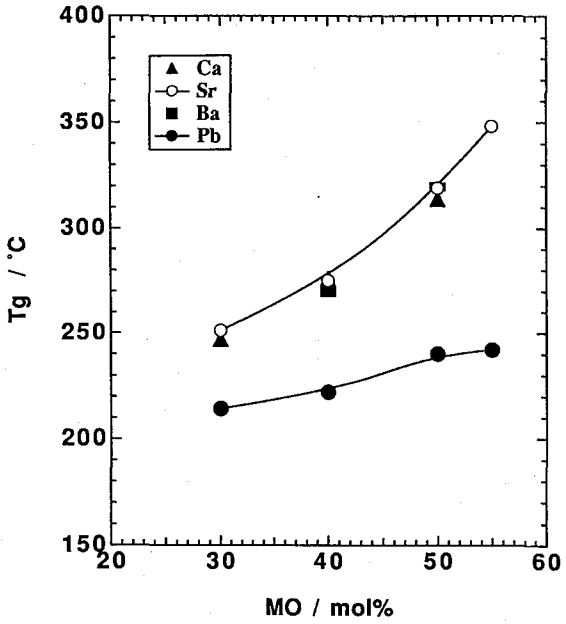

Fig. 2. Plots of the T_g vs. the MO content for divalent metal vanadate glasses.

In Fig. 2 the T_g is plotted against the MO content. It is seen that in every glass system the T_g values of glasses increase with increasing MO content.

3.3 Crystallization behavior

The XRD profiles of two glass systems, $xSrO{\cdot}(100\text{-}x)V_2O_5$ (x=30, 40, 50) and $xPbO{\cdot}(100\text{-}x)V_2O_5$ (x=30, 40, 50) after heat-treatment at various temperatures are shown in Fig. 3 and 4, respectively. Table 3 summarizes the crystalline phases precipitated from the glass samples heated at different temperatures in air. For $50SrO{\cdot}50V_2O_5$ glass, many distinct peaks due to $Sr(VO_3)_2$ crystal were observed when heat-treated at 450°C for 1 hour. When the heat-treatment time was extended up to 120 hours, the diffraction peaks due to new $Sr(VO_3)_2$ crystalline phase appeared. For $40SrO{\cdot}60V_2O_5$ glass, $Sr(VO_3)_2$ crystals first precipitated at 350°C, followed by the precipitation of VO_2 crystals and unknown phases at 500°C. For $30SrO{\cdot}70V_2O_5$ glass, $V_3O_7{\cdot}H_2O$ crystals first precipitated at 300°C and grew up to 350°C. At 500°C clear peaks due to VO_2 crystals were observed together with those due to unknown phases, but $V_3O_7{\cdot}H_2O$ crystals were no longer present.

For $50PbO{\cdot}50V_2O_5$ glass, many distinct peaks due to $Pb(VO_3)_2$(III)[3] and $Pb_2V_2O_7$

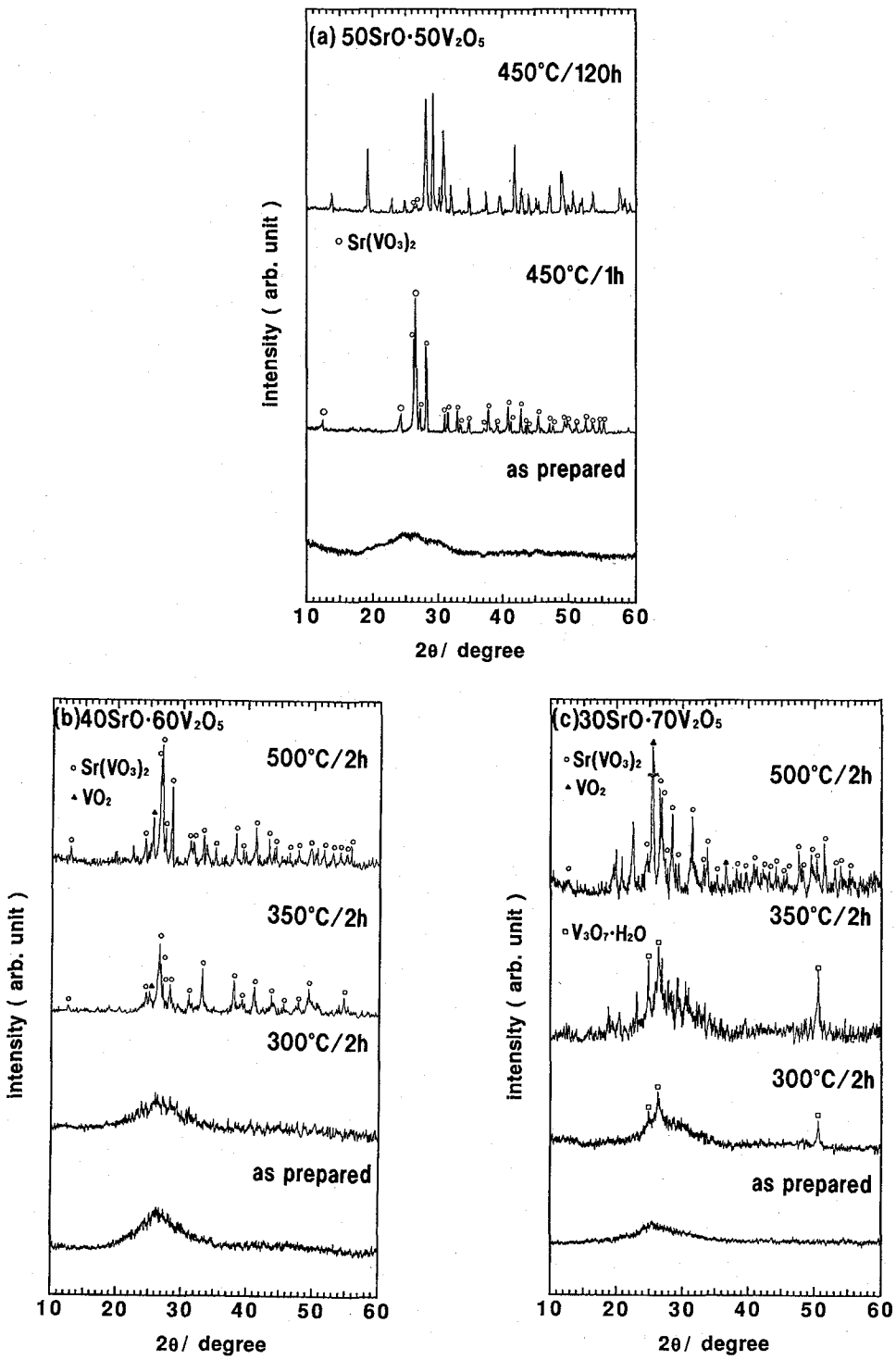

Fig. 3. X-ray diffraction patterns of (a) $50SrO{\cdot}50V_2O_5$, (b) $40SrO{\cdot}60V_2O_5$ and (c) $30SrO{\cdot}70V_2O_5$ glasses before and after heat-treatment.

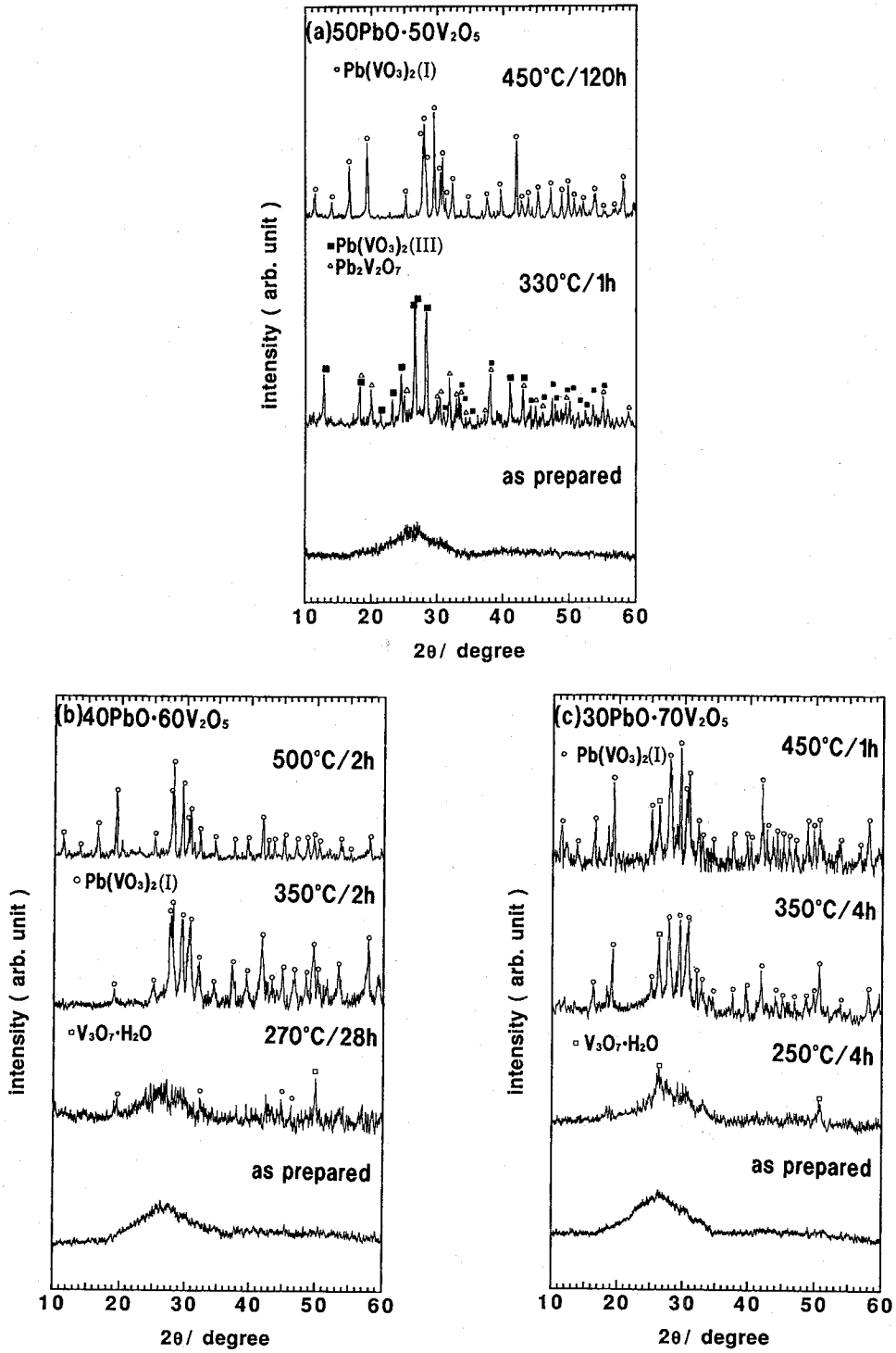

Fig. 4. X-ray diffraction patterns of (a) $50PbO \cdot 50V_2O_5$, (b) $40PbO \cdot 60V_2O_5$ and (c) $30PbO \cdot 70V_2O_5$ glasses before and after heat-treatment.

Table 3. Characterization of annealed $SrO-V_2O_5$ and $PbO-V_2O_5$ glass samples.

Annealing temperature/°C	Phase		
	$50SrO \cdot 50V_2O_5$	$40SrO \cdot 60V_2O_5$	$30SrO \cdot 70V_2O_5$
as-prepared	Am[a)]	Am	Am
300	—	Am	Am, $V_3O_7 \cdot H_2O$
350	—	$Sr(VO_3)_2$	$Sr(VO_3)_2$, VO_2, $V_3O_7 \cdot H_2O$
450	$Sr(VO_3)_2$	—	—
500	—	$Sr(VO_3)_2$, VO_2, Un[b)]	$Sr(VO_3)_2$, VO_2, Un
	$50PbO \cdot 50V_2O_5$	$40PbO \cdot 60V_2O_5$	$30PbO \cdot 70V_2O_5$
as-prepared	Am	Am	Am
250	—	—	Am, $Pb(VO_3)_2$(I), $V_3O_7 \cdot H_2O$
270	—	Am, $Pb(VO_3)_2$(I), $V_3O_7 \cdot H_2O$	—
330	$Pb_2V_2O_7$, $Pb(VO_3)_2$(III)	—	—
350	—	$Pb(VO_3)_2$(I), $V_3O_7 \cdot H_2O$	$Pb(VO_3)_2$(I), $V_3O_7 \cdot H_2O$, Un
450	$Pb(VO_3)_2$(I)	—	$Pb(VO_3)_2$(I), $V_3O_7 \cdot H_2O$, Un
500	—	$Pb(VO_3)_2$(I), Un	—

a) Am: amorphous phase, b) Un: unknown crystalline phase.

crystals were observed when heat-treated at 330°C between T_{x1} and T_{x2}. At 450°C the diffraction peaks from $Pb_2V_2O_7$ crystals were no longer observed and instead those from $Pb(VO_3)_2$(I)[4] crystals were observed. For $40PbO \cdot 60V_2O_5$ glass, the diffraction peaks due to $V_3O_7 \cdot H_2O$ and $Pb(VO_3)_2$(I) crystals were observed at 270°C. The $Pb(VO_3)_2$ crystals grew on heating to 500°C, while the $V_3O_7 \cdot H_2O$ crystals disappeared. For $30PbO \cdot 70V_2O_5$ glass, the diffraction peaks due to $V_3O_7 \cdot H_2O$ crystal were observed together with the small peaks due to $Pb(VO_3)_2$(I) crystal at 250°C. When the heat-treatment temperature was raised above 350°C, $Pb(VO_3)_2$(I) crystals became a major crystalline phase.

4. DISCUSSION

4.1 Glass transition temperature

The T_g values of alkaline earth vanadate glasses are found to be almost the same irrespective of the kind of the alkaline earth cation. This well corresponds to our previous finding that the structure of alkaline earth vanadate glasses are very similar to each other irrespective of the kind of the alkaline earth cation.[1,2]

Another interesting finding is that the T_g increases with increasing content of modifier, MO. Recently, we have determined the compositional changes of different vanadate groups present in alkaline earth metal and lead vanadate glasses based on the ^{51}V NMR measurements.[2] Figure 5 shows the results for (a) $SrO-V_2O_5$ and (b) $PbO-V_2O_5$ glasses. The fractions of $V_2O_7^{4-}$ groups and $(VO_3)_n$-single chains increase with increasing MO while those of branched-VO_4 tetrahedra and $(V_2O_8)_n$-zigzag chains decrease. It therefore follows that the coexistence of $V_2O_7^{4-}$ groups and $(VO_3)_n$-single chains increase the stability of vanadate glasses probably due to the increased randomness. Contrarily, the presence of $(V_2O_8)_n$-zigzag chains or three dimensional corner-sharing branched VO_4-tetrahedral groups lowers T_g. This result may be

explained as follows. Tsuzuki et al.[5] have shown that amorphous V_2O_5 film crystallizes at very low temperature of 210°C without a glass transition. This indicates that the branched-VO_4 groups transform into $(V_2O_8)_n$-zigzag chains at relatively low temperatures, because the thermodynamic stability of the former is low at low temperatures.

It is noted that the T_g's of lead vanadate glasses are very low compared with those of alkaline earth vanadate glasses. This is possibly because the fraction of thermodynamically unstable $(V_2O_8)_n$-zigzag chains is much smaller in SrO-V_2O_5 glasses than in PbO-V_2O_5 glasses.

4.2 Crystallization behavior of SrO-V_2O_5 and PbO-V_2O_5 glasses

In V_2O_5-rich glass ($x=30$) the crystalline phases precipitated from the glasses were mainly $M(VO_3)_2$ and VO_2, although several unknown phases were precipitated. The diffraction peaks due to $V_3O_7{\cdot}H_2O$ crystal were observed at lower temperature of 270–300°C, indicating that the V_2O_5-rich phases are present in the glass sample. The formation of hydrated phase, such as $V_3O_7{\cdot}H_2O$ are explained as follows. The first precipitating phase, $V_3O_7{\cdot}H_2O$, is formed by the reaction of the V_2O_5-rich phase with a small amount of H_2O present in the glass as well as

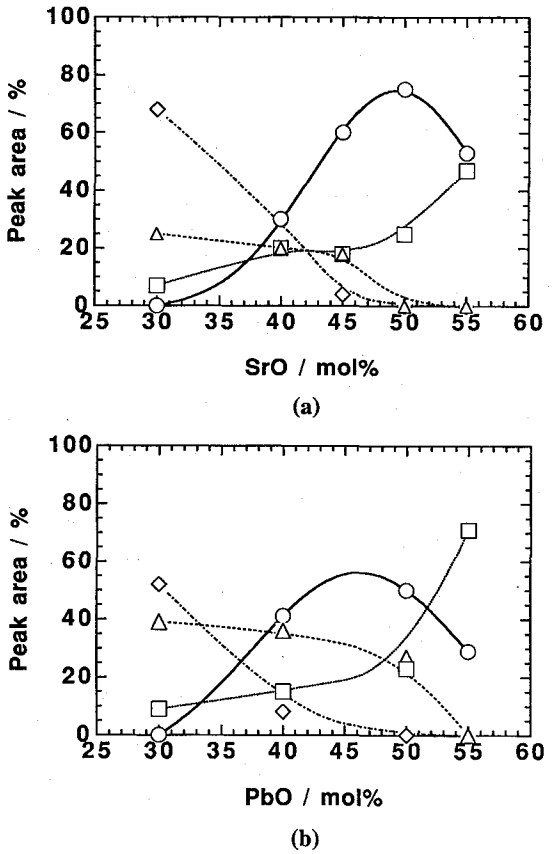

Fig. 5. Plots of the percentage of the vanadate groups in several vanadate glasses vs. the MO content(M=Sr, Pb). (a) SrO-V_2O_5, (b) PbO-V_2O_5. ·····□·····: $V_2O_7^{4-}$, —○—: $(VO_3)_n$-single chain, -·-◇-·-: branched-VO_4 group, ---△---: $(V_2O_8)_n$-zigzag chain.

moisture in ambient atmosphere. As described in previous study,[1] the $V_3O_7{\cdot}H_2O$ phase is readily formed by the reaction between V_2O_5-rich glass and H_2O from ambient moisture even at room temperature.

In $40MO{\cdot}60V_2O_5$ glasses the crystalline phases precipitated from the glasses were mainly $M(VO_3)_2$ and VO_2. It is noted that in $40SrO{\cdot}60V_2O_5$ glass the diffraction peaks due to VO_2 crystal are very intense. In $40PbO{\cdot}60V_2O_5$ glass the diffraction peaks due to $V_3O_7{\cdot}H_2O$ crystal were observed at 270°C, indicating that the V_2O_5-rich phases are present in the glass sample. On the other hand, the diffraction peaks due to $V_3O_7{\cdot}H_2O$ crystal were not observed in $40SrO{\cdot}60V_2O_5$ glass, indicating that the fraction of the V_2O_5-rich phases of $40SrO{\cdot}60V_2O_5$ glass is small compared with that of $40PbO{\cdot}60V_2O_5$. This is in good agreement with the result of NMR study in Fig.5.

In $50SrO{\cdot}50V_2O_5$ glass, $Sr(VO_3)_2$ crystals were first precipitated on heating at 450°C for 1 hour and then transformed into new $Sr(VO_3)_2$ crystal on further heating at 450°C for 120 hours. This indicates that crystallization proceeds as follows:

at 450°C for 1 hour

$$\underset{\text{amorphous}}{50SrO{\cdot}50V_2O_5} \rightarrow \underset{\text{crystal}}{Sr(VO_3)_2} \qquad (1)$$

and for 120 hours

$$\underset{Pb(VO_3)_2(III)\text{-type}}{Sr(VO_3)_2} \xrightarrow{\text{phase transition}} \underset{Pb(VO_3)_2(I)\text{-type}}{\text{new } Sr(VO_3)_2} \qquad (2)$$

Therefore, it is found that $Sr(VO_3)_2$ crystal first precipitated out of metavanadate glasses is a metastable and high temperature phase, while new $Sr(VO_3)_2$ crystal is a stable and low temperature phase. The metastable $Sr(VO_3)_2$ crystal consists of $(VO_3)_n$-single chains and its structure is very similar to that of $Ba(VO_3)_2$ and $Pb(VO_3)_2$(III) crystals. However, at temperatures just below the crystallization temperature metastable $Sr(VO_3)_2$ crystal is transformed into stable new $Sr(VO_3)_2$ crystal. The structure of new $Sr(VO_3)_2$ crystal is assumed to be identical to that of $Pb(VO_3)_2$(I) crystal consisting of $(V_2O_8)_n$-zigzag chains, because their X-ray diffraction patterns are very similar to each other, and the profiles and peak positions of their infrared spectra, which are not shown here, are also very similar to each other. The structural analysis of this crystal will be made elsewhere.

In $50PbO{\cdot}50V_2O_5$ glass, first $Pb(VO_3)_2$(III) and $Pb_2V_2O_7$ crystals are precipitated by heating at 330°C and then transformed into single phase, $Pb(VO_3)_2$(I) crystal on heating to 450°C. Taking into account the glass composition, this indicates that the crystallization proceeds as follows:

at 310°C

$$\underset{\text{amorphous}}{50PbO{\cdot}50V_2O_5} \rightarrow \underset{\text{crystal}}{Pb(VO_3)_2(III)} + \underset{\text{crystal}}{Pb_2V_2O_7} + \underset{\text{amorphous}}{V_2O_5} \qquad (3)$$

and at 390°C

$$\underset{Pb(VO_3)_2(III)}{} \xrightarrow{\text{phase transition}} \underset{Pb(VO_3)_2(I)}{} \qquad (4)$$

$$\underset{\text{crystal}}{Pb_2V_2O_7} + \underset{\text{amorphous}}{V_2O_5} \rightarrow \underset{\text{crystal}}{Pb(VO_3)_2(I)} \quad (5)$$

As seen from Fig. 5(b), $50PbO{\cdot}50V_2O_5$ glass consists of many kinds of vanadate groups, such as $V_2O_7^{4-}$, $(VO_3)_n$-single chains and $(V_2O_8)_n$-zigzag chains. This can be expressed by the following equilibrium reactions:

$$\underset{\text{Vanadate group: } (VO_3)_n\text{-single chain}}{Pb(VO_3)_2} \rightleftharpoons \underset{V_2O_7^{4-}}{Pb_2V_2O_7} + \underset{(V_2O_8)_n\text{-zigzag chain}}{V_2O_5}. \quad (6)$$

In $50PbO{\cdot}50V_2O_5$ glass, the equilibrium is shifted to the left to a considerable extent as known from Fig. 5(b). This may be related to the fact that $Pb(VO_3)_2$(I) crystal melts incongruently at 482°C[6], that is, $Pb(VO_3)_2$ is not thermodynamically stable at high temperatures. It can be therefore concluded that the $Pb_2V_2O_7$ crystal and metastable $Pb(VO_3)_2$(III) crystal are precipitated directly from the corresponding vanadate groups present in the glass. The low temperature stable phase, $Pb(VO_3)_2$(I), is mainly formed as a result of the phase transition of $Pb(VO_3)_2$(III) crystal. Since in $50SrO{\cdot}50V_2O_5$ glass the glass network consists of only $(VO_3)_n$-single chains, a single phase of metastable $Sr(VO_3)_2$ crystal is precipitated from the beginning.

5. CONCLUSION

The glass-forming region and glass transition and crystallization temperatures for binary divalent metal vanadate glasses have been discussed. The following conclusions were drawn.

(1) The T_g and the T_x of alkaline earth metavanadate glasses are almost the same irrespective of the kind of the alkaline earth metal.

(2) The T_g values of lead vanadate glasses are small compared with those of alkaline earth vanadate glasses.

(3) The V_2O_5-rich phase readily crystallizes as the hydrate, $V_3O_7{\cdot}H_2O$, from vanadate glasses by the reaction with a small amount of H_2O in the glass and in ambient atmosphere.

(4) As for $50MO{\cdot}50V_2O_5$ glasses (M=Sr, Pb), the process of crystallization depends on the vanadate groups present in these glasses.

6. ACKNOWLEDGMENTS

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